SYMPOSIUM ON NEW CATALYTIC MATERIALS
PRESENTED BEFORE THE DIVISION OF FUEL CHEMISTRY
AMERICAN CHEMICAL SOCIETY
MIAMI MEETING, SEPTEMBER 10-15,1989

OLIGOMERIZATION OF ISO-BUTENE WITH AN IMPROVED CATALYST

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INTRODUCTION

In conversion processes in oil refining LPG (C_3 and C_4) are formed as byproducts. When catalytic cracking is used the LPG will have a high content of unsaturated components. The low price of the LPG, compared to gasoline, makes oligomerization of the molecules in LPG worthwhile for the industry. There are mainly two processes used in the refineries for this purpose. In alkylation, liquid sulphuric or hydrofluoric acids are employed and in the other process phosphoric acid on silica or diatomeric earth. In the refining industry the latter process is normally called polymerization, although dimerization is the dominating and most wanted reaction. In the alkylation process iso-butene is reacted with either propane or butane. If using the less strong phosphoric acid, two alkenes must be used as reactants and at a higher temperature. The mounted phosphoric acid catalyst leaks less acid to downstream processing and therefore gives less severe corrosion problems than with alkylation (1). The chemistry of the oligomerization can be shown as:

$$C = C - C \quad + \quad H^+ \longrightarrow C - C^+ - C$$

$$C - C^+ - C \quad + \quad C = C - C \longrightarrow \begin{matrix} C \\ C \end{matrix} > C - \overset{+}{C} < \begin{matrix} C \\ C \end{matrix}$$

$$\begin{matrix} C \\ C \end{matrix} > C - \overset{+}{C} < \begin{matrix} C \\ C \end{matrix} \longrightarrow {-H^+} \longrightarrow C_6H_{12} \text{ - isomers}$$

The formed carbonium ions and hexenes can react further to trimers and higher. The phosphoric acid on silica catalyst is also an important catalyst for the production of petrochemical intermedates like nonene and alkylaced aromates.

The traditional method of producing the mounted phosphoric acid on silica is to start from kiesel guhr and phosphoric acid. The water content of the phosphoric acid should be low so that the final catalyst contains 65-70% by weight of P_2O_5. The mixture is extruded or bricketted, dried, calcined and finally hydrated to a preferred level, usually with steam. There are several proposals in the patent literature to improve the mechanical strength of the final product. One method is to steam treat the mixture before extrusion (2). It is also possible to add bentonite, montmorillonite, halloysite, or other compounds to the mixture before extrusion. The acidity of the catalyst can also be reached by using an aluminum silicate or zeolite instead of the above mentioned acids. The kiesel guhr carrier can be replaced by a silica hydrogel (3,4). Recently Bernard et al (5) proposed to extrudate the silica carrier before impregnating the phosphoric acid. Little interest has been shown in the development of new or improved catalysts for oligomerization of propene and butene in the recent literature. It is therefore of interest to use modern analytical instruments to explain and improve the catalyst. In this paper, an improved catalyst based on mounted phosphoric acid on silica will be presented.

EXPERIMENTAL

The used silica carriers were spheres with a diameter of 2.2 mm, received from Shell Corp. in London. In Table 1, more details of pore volumes and pore sizes are presented. The phosphoric acid used was of pro analysi quality form Kebo Lab. (Sweden) and the iso-butene from AGA Gas Ltd. (Sweden).

The catalysts were made by combining the following steps in different sequences: Impregnation with phosphoric acid of 42% by weight of P_2O_5 or other concentrations if indicated. Drying at 170°C for 5 hrs. and calcining in a muffle furnace for 4 hrs. at various temperatures. Some catalysts were steamed at 100°C in 100% steam.

Testing of the activity of the catalysts was done in a 23 cc stainless steel reactor with iso-butene in vapour phase. A constant contact time of 1.00 hr. was maintained in all experiments by measuring and controlling the inlet flow. In Figure 1, a simple flow diagram of the reaction system is presented. Temperature, pressure and gas flow were kept constant at 160°C, 1 atm and 12.5 g of iso-butene per hour, respectively. The yields were determined by measuring the weight of liquid products and the amount of iso-butene feed. The liquid products were analyzed on GC with FID detector and the simulated distillation was made according to ASTM D2887-3. BET pore volume and surface area were measured with Micromeritics Digisorb 2600.

RESULTS AND DISCUSSION

In Table 2, the BET surface area and pore volumes of the silica spheres used are presented. The pore volume determined with the BET method is considerably different from the pore volumes presented by the manufacturer of the silica spheres (Table 1). The main difference is probably due to macro pores not detected by the BET method.

Impregnation of the silica sphere I with different acid concentrations followed by drying at 170°C, did not effect the initial activity of the final catalyst. However, after 20 hrs. of experiment, catalyst produced by impregnating higher concentrations of phosphoric acid showed a lower conversion (Table 3). In spite of this it is important to use a higher concentration of the acid in order to reach a P_2O_5 concentration of 65-70% in the final catalyst. On the other hand, too high a viscosity, which is found in concentrated phosphoric acid, reduces the impregnation speed.

In Figure 2, the conversion as a function of time is presented for three different catalysts produced from the three different silica spheres by the same procedure. Calcination was done at 425°C. The catalyst produced from silica spheres III, with both larger pores and pore volume compared with silica spheres II, gives the highest activity. The conversion was 78% after 20 hrs. of experiment. The catalyst produced from silica sphere II, gives a better conversion than does the catalyst produced from silica sphere I. Thus the selection of silica carrier should be; large average pores and large pore volumes.

In Figure 3 the effect on activity of calcining at 350°C and 425°C is presented. The higher temperature gives a lower activity and calcining at 350°C gave a catalyst with a conversion of 97,6%. This catalyst also maintained the conversion level in an experiment of over 70 hrs. In a separate experiment silica spheres were calcined at 550°C, before impregnation without affecting the conversion of the final product. Calcining after impregnation effects the bindings between phosphoric acid and the silanol groups and dehydration of the phosphoric acid. As no effect of calcining at 550°C before impregnation was noted, the silanol groups of the silica remained intact. If only one impregnation is carried out, the activity of the final catalyst drops quickly after a few hours of the experiment (Table 3). When water is added in the feed, or the catalyst is wetted with water, the activity rises again for a short period. This indicates that the phosphoric acid bound to the silica is not as active as free acid in the catalyst. It is probably due to the fact that bound acid does not have the same capacity to retain water as free acid. The high sensitivity of water content in the feed makes the catalyst, which has been impregnated once only, impractical for commercial use.

In Figure 4 the activity of commercial catalyst is plotted as a function of time. The ground catalyst shows a much higher conversion rate (66%) after 20 hrs of experiment than the unground catalyst (18%). In the small reactor used, the unground catalyst will give large wall effects due to the small dimensions of the reactor. The ground catalyst has a lower activity compared to the best of the catalysts produced in this study. In the production of gasoline a dimer or trimer is wanted, while the formation of tetramers is not wanted since they normally fall outside the gasoline boiling range. The selectivity of some catalysts is presented in Table 4. For catalysts with high conversions, the formation of tetramers is also high. The catalyst calcined at 350°C shows an acceptable selectivity (dimer + trimer = 96%) and at the same time conversion 98%. The unground commercial catalyst shows 4.3% tetramers in the liquid while the ground catalyst only shows 2.8%. The higher production of tetramers is probably an effect of large pore diffusion times of the primary dimer in the unground catalyst. The yield of trimeres follows the same pattern as the yield of tetrameres.

CONCLUSIONS

A high activity oligomerization catalyst based on phosphoric acid on silica has been produced by impregnation of silica spheres. A calcining temperature of 350°C is more better than calcining at 450oC or only drying at 170°C. The catalyst has a low sensitivity to water concentration in the feedstock provided it has been impregnated twice with calcination between. The activity of the catalyst produced by impregnation is higher than that of the commercial catalysts used in this study.

REFERENCES

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Table 1. Silica spheres. Properties according to manufacture.

ID	Pore Volume ml/g	Average Pore Size, Angstroms
I	1.0	300
II	1.0	600
III	1.3	600

Table 2. Silica spheres. Analytical results.

ID	Pore volume BET ml/g	Surface Area m^2/g	Bulk Density g/cm^3
I	0.95	79	0.43
II	0.77	62	0.40
III	0.72	60	0.36

Table 3. Conversion expressed as weight percent conversion after 20 hrs. of experiment with iso-butene. Impregnation with different acid concentrations in one step without calcination.

% P_2O_5	Conversion
6	20
11	22
21	17
42	6
85	9

Table 4. Selectivities

Catalyst	Time on Stream h	Weight % in Liquid di-	tri-	tetra-	Conversion Weight %
Spheres III, calc 425	3	74.9	22.1	3.0	88.6
Spheres III, calc 425	23	84.0	14.9	1.1	79.6
Spheres III, calc 425	47	84.4	14.6	1.0	79.6
Spheres III, calc 350	27	73.3	22.7	4.0	97.6
Commercial unground	49	68.5	27.2	4.3	16.9
Commercial ground	49	76.5	20.7	2.8	65.4

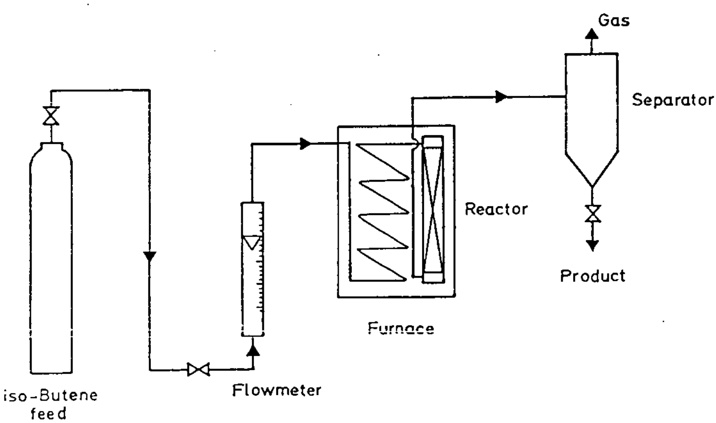

Figure 1. Simple flow diagram of reaction system.

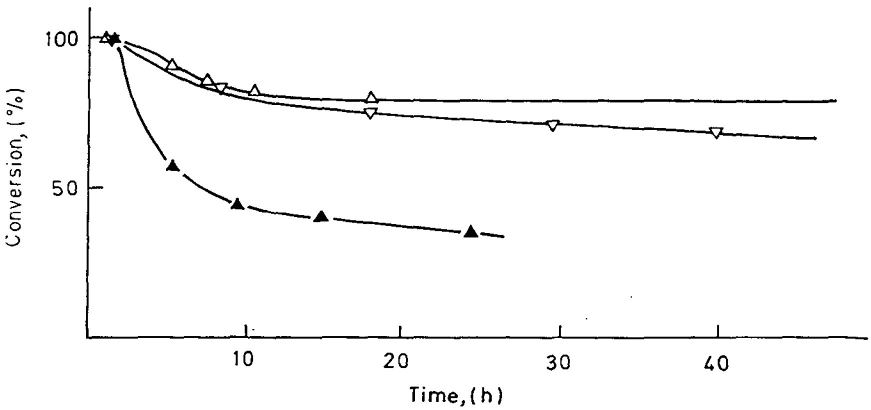

Figure 2. Conversion in weight percent of catalysts prepared with silica spheres I ▲, II ▽ and III △. Calcined at 425°C and impregnated twice.

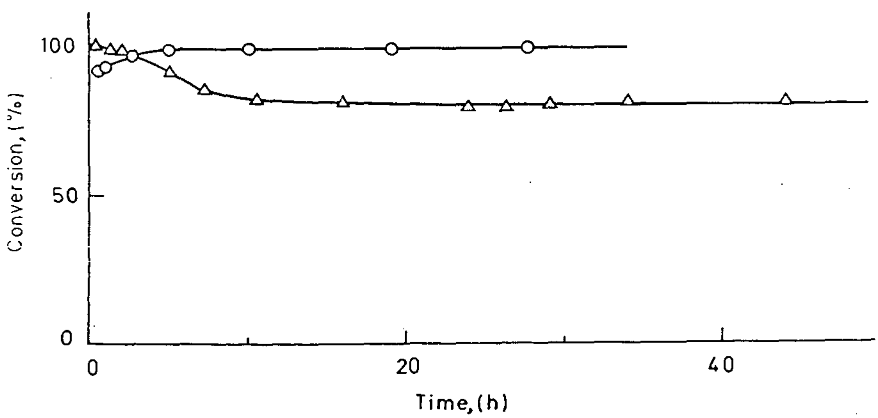

Figure 3. Conversion in weight percent of catalysts calcined at 350°C ○ and 425°C △. Catalysts prepared from sphere III, impregnated with phosphoric acid (42%, P_2O_5), calcined, impregnated and dried.

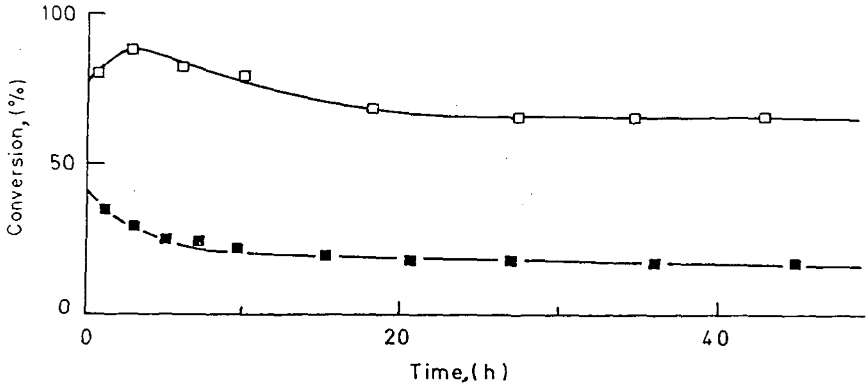

Figure 4. Conversion of commercial catalyst in weight percent. Unground ■ and ground □.